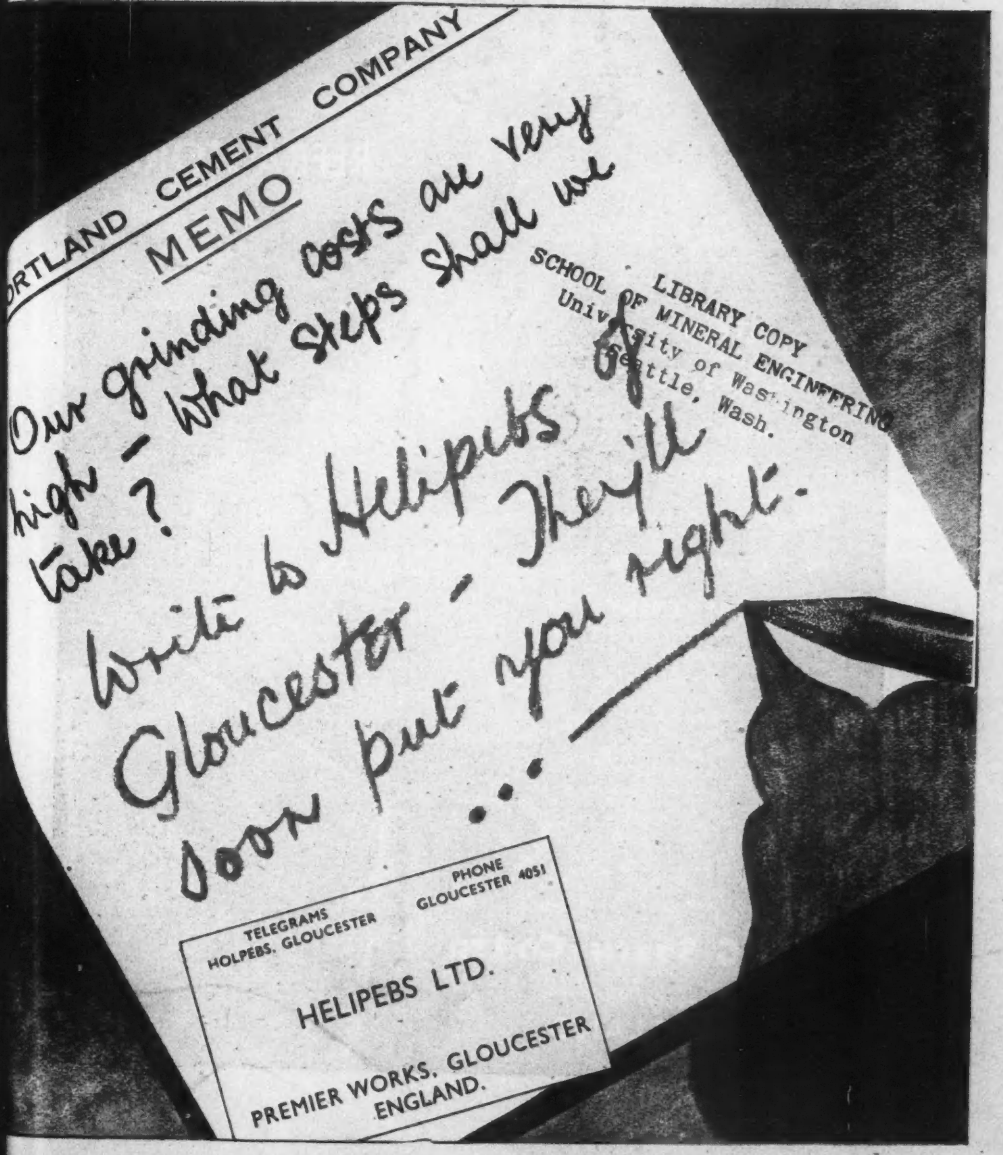
691.5
C&EM

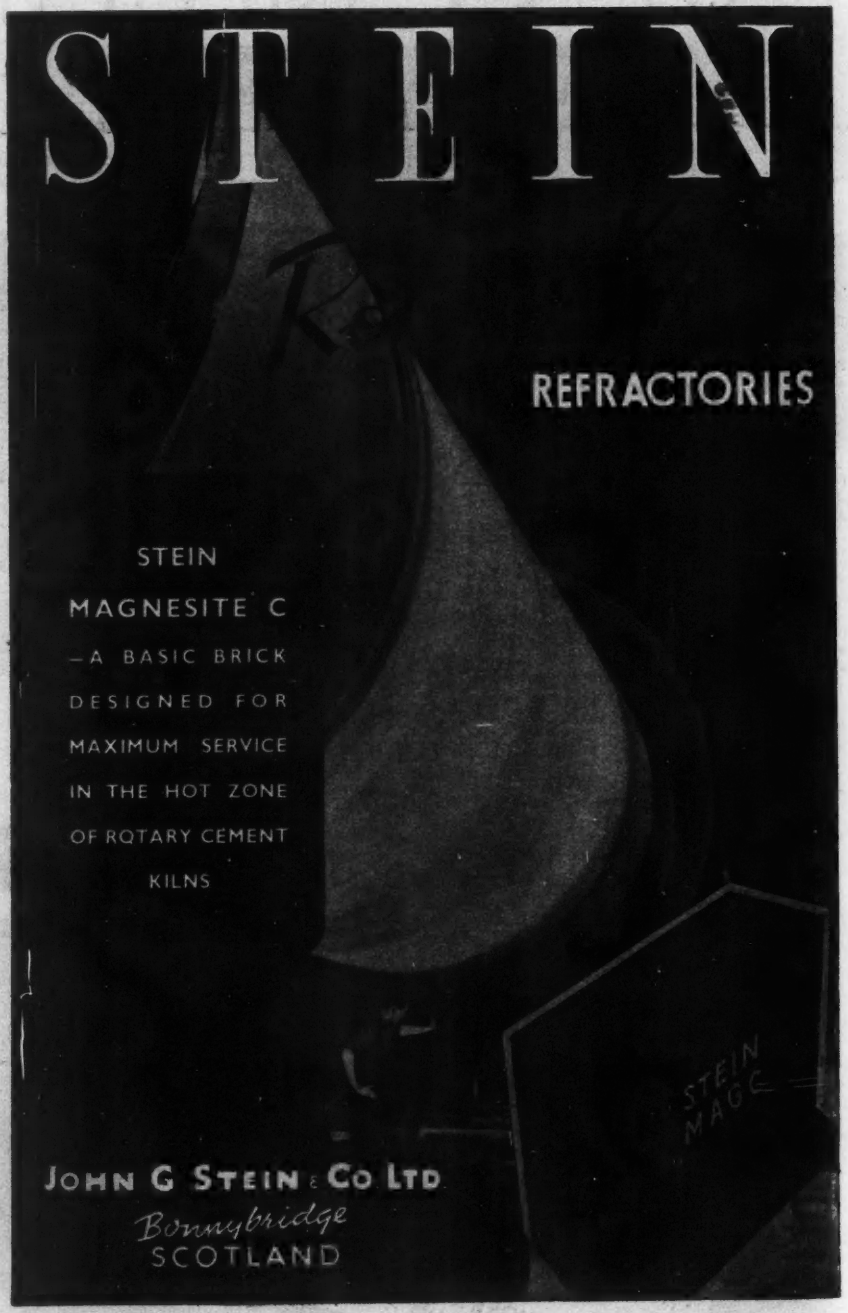
CEMENT AND LIME MANUFACTURE

UNI... LIBRARY
...INGTON
APR 13 1948
...ATTLE, WASHINGTON

Vol. XXI. No. 2 MARCH 1948 PRICE 1/- ALTERNATE MONTHS


PORTLAND CEMENT COMPANY
MEMO
Our grinding costs are very high - What steps shall we take?
Write to Helipebs Gloucester - They'll soon put you right ...
SCHOOL OF MINERAL ENGINEERING
University of Washington
Seattle, Wash.
LIBRARY COPY
TELEGRAMS HOLPEBS, GLOUCESTER
PHONE GLOUCESTER 4051
HELIPEBS LTD.
PREMIER WORKS, GLOUCESTER ENGLAND.

PUBLISHED BY CONCRETE PUBLICATIONS LTD., 14, DARTMOUTH STREET, LONDON S.W.1


STEIN
REFRACTORIES
STEIN
MAGNESITE C
—A BASIC BRICK
DESIGNED FOR
MAXIMUM SERVICE
IN THE HOT ZONE
OF ROTARY CEMENT
KILNS
STEIN
MAGC
JOHN G STEIN & CO LTD
Bonnybridge
SCOTLAND

CEMENT AND LIME MANUFACTURE

PUBLISHED ALTERNATE MONTHS. PRICE 1/- A COPY. ANNUAL SUBSCRIPTION 6s. POST FREE.

PUBLISHED BY
CONCRETE PUBLICATIONS LIMITED
14 DARTMOUTH STREET, LONDON, S.W.1

TELEPHONE: WHITEHALL 4581.
TELEGRAPHIC ADDRESS:
CONCRETIUS, PARL, LONDON.

PUBLISHERS OF
"CONCRETE & CONSTRUCTIONAL ENGINEERING"
"CONCRETE BUILDING & CONCRETE PRODUCTS"
"CEMENT & LIME MANUFACTURE"
"THE CONCRETE YEAR BOOK"
"CONCRETE SERIES" BOOKS, ETC.

VOLUME XXI. NUMBER 2 MARCH, 1948

New Process in Lime Manufacture.

A NEW process in lime manufacture, based on the fact that fine powders may be kept in suspension in air or other gas as in the Fuller-Kinyon pump, as being operated by the New England Lime Co., at Adams, Mass., U.S.A., is described by Mr. W. C. Lenhart and Mr. N. C. Rockwood in "Rock Products" for January, 1948. This principle is used to carry out chemical reactions, including the calcination of fine particles of limestone or other forms of calcium carbonate. The principle was first applied to the "fluid-solid catalyst" process of producing high-octane petrol during the war, and the Dorr Company is licensed to apply the process to some other industries. A limitation of the system is that it must be possible to effect the intended reaction at temperatures that do not soften or fuse the solids during treatment.

As used for calcining limestone the system is a continuous one in which finely-ground materials are fed into the top of the reactor or furnace (*Fig.* 1) and the calcined and relatively cool product withdrawn continuously at the bottom. The reaction takes place in the reactor which replaces kilns of the type generally used. The period of treatment in the reactor is that required for the average size of particle; in this instance it is adjusted to calcine 95 to 99 per cent. of the total. The passage of the stone through the reactor is such that in many cases the original physical structure of the stone is retained in the lime. The wear and tear on the brickwork and the constriction plates is said to be very little, and the pilot kiln shows that ordinary fire-clay brick lining is hardly damaged after 11 months of intermittent use.

The limestone particles are kept in suspension at a temperature higher than the ignition temperature of the fuel used in the calcination chamber. When the fuel is injected it burns on and around the particles, under the most favourable conditions for heat transfer. The temperature can be controlled with accuracy by the amount of stone and fuel and the amount of air admitted for keeping the

material in suspension, which determines the time required for keeping the material at any desired temperature. All these factors are controlled by instruments which, with experience, become almost automatic in operation.

As the result of experience gained in the operation of this 5-ft. by 26-ft. (inside dimensions) reactor designed for a capacity of 8½ tons per 24-hour day, designs have been completed and installation will soon be made of a similar reactor having a capacity of 100 tons per day. The pilot reactor has produced up to 15 tons per day, operating best at 11 tons and with a consumption of about 42 gallons of fuel oil, or about 6,250,000 B.T.U., per ton of lime. Since a ton of good bituminous coal contains about 28,000,000 B.T.U., this is the usual ratio of about 1 : 4½.

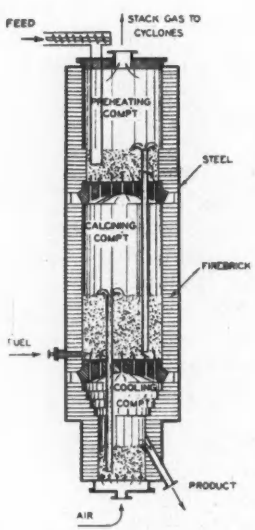


Fig. 1.—The Pilot Reactor.

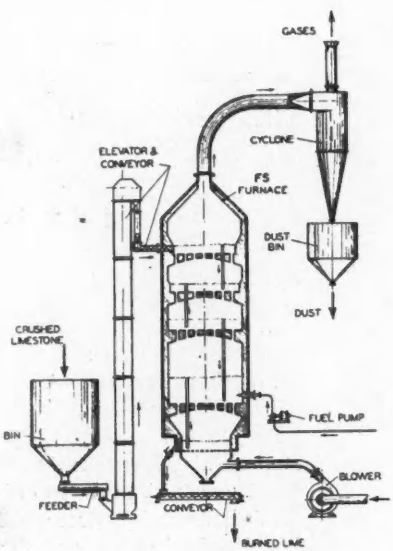


Fig. 2.—Flow Sheet of Five-Compartment Reactor.

The pilot reactor is a steel-shell cylinder approximately 7 ft. by 26 ft. lined with refractory bricks 9 in. thick and with 3 in. of insulation between these and the steel shell. Like a shaft kiln, the pilot reactor has three zones—preheating, calcining, and cooling—but in this case the zones are actual compartments separated from one another by perforated domed refractory partitions, or constriction plates, as shown in *Fig.* 1. The proportioning of these compartments might be varied for different raw materials. The 100-ton reactor will be a steel cylinder, with conical ends, measuring about 13½ ft. by 42 ft. and divided into five compartments, instead of three, as shown in *Fig.* 2. *Figs.* 3 and 4 are views of the pilot reactor.

The three compartments of the pilot reactor are formed by constriction plates of arched fire-brick construction. In each plate are holes for the passage of gases. The raw material is fed in at the top by a screw conveyor through a steel feed pipe which extends to near the bottom of the top compartment. The outlet of this compartment is through a similar tube that extends through the constriction plate to near the bottom of the second compartment (the calcining zone). Thus the top compartment is always full to a pre-determined level, and as stone is admitted to this compartment an equal amount is discharged to the compartment below.

The three compartments, (1) preheater, (2) combustion and calcining, and (3) the cooler, contain a predetermined amount of material. In starting the reactor,

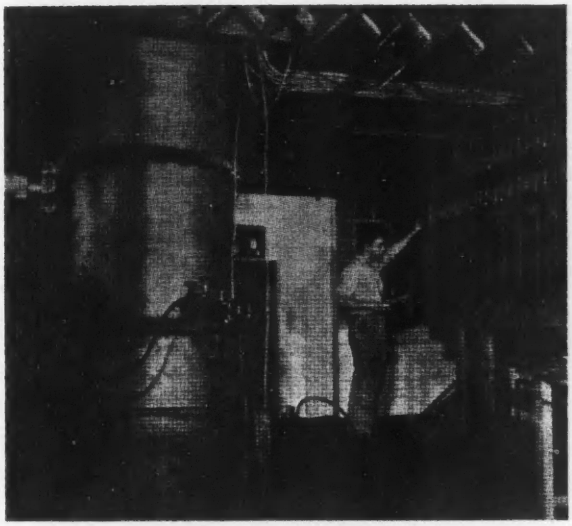


Fig. 3.—The Operating Floor.

a large torch is fired into the air stream in the bottom to preheat the limestone to the ignition point of the fuel oil (about 1100 deg. F.). When the stone in the combustion zone is at this temperature, fuel oil is injected into the mass, without spraying, through eight nozzles equally spaced around the periphery and near the bottom of the combustion compartment. A rotary compressor supplies the air. With the great excess of hot surface area available, combustion is complete, and is adjacent to and on the surface of the limestone particles. All of the air for combustion is thus supplied and preheated in cooling the lime.

The depth of the charge in the combustion zone can be varied, but regardless of the depth of the charge the temperature has been found to be practically the

same throughout. The amount of oil from each injection tube is controlled by an 8-cylinder piston-type adjustable pump that delivers the same amount of oil to each tube. The total amount of oil going to the furnace is controlled by a variable-speed motor of wide range. As the temperature rises, an increase in the flow of stone keeps the temperature at the desired point. In the pilot reactor it was found that 1700 deg. F. was about suitable for most limes. The temperature of the stone entering the calcining compartment is about 1100 deg. F. In each compartment there is a certain amount of free space above the material; this space varies with the nature of the products being treated, but is chiefly intended for settling some of the dust entrained in the hot gases.

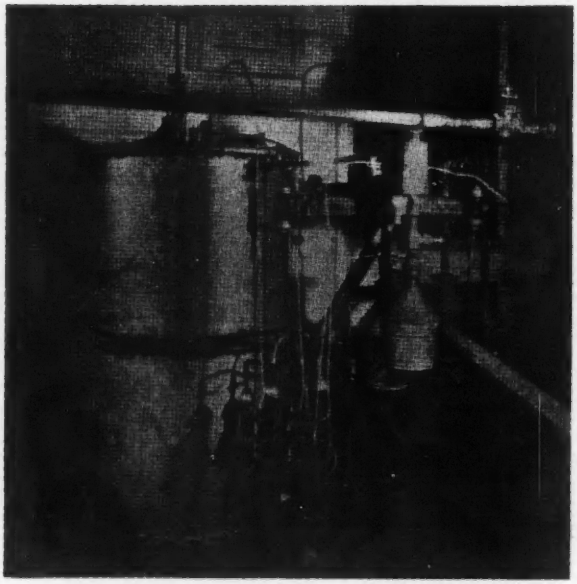


Fig. 4.—Upper Part of Reactor.

It is impossible to see into the reactor while it is in operation. Control is by eight monometers that indicate the amount of material in each compartment. Recording pyrometers show the temperatures of the fluid-solid mass in the reactor, which is closer to the actual calcining temperatures than can be measured in other types of kilns. A vibrating feeder controls of the amount of the feed.

Where finely-divided coal is used for fuel it is expected that equivalent fuel ratios will be obtained. Thus the fuel consumption is equal to modern shaft kilns (6,500,000 B.T.U. per ton). Radiation losses were about 13 per cent., but in larger reactors it is hoped to reduce this considerably. Dust losses on the minus 6-mesh—plus 80-mesh feed were from the 5 to 10 per cent.; this dust is collected in four small collectors of the cyclone type operating in parallel.

Calcination depends on the average time each particle is in the reactor, and this can be calculated and controlled. In the pilot plant the cooling zone lowered the temperature of the discharged product to about 500 deg. F. The tubes used for the passage of the materials from compartment to compartment are of stainless steel, and have a long life at 2000 deg. F.

In the pilot plant temperature controls could be exercised to a remarkable degree and the minus 6-mesh—plus 80-mesh stone could be calcined at temperatures near the theoretically correct temperatures. This has resulted in limes that are remarkably active. However, higher temperatures can be used, enabling the production of harder-burned material. It has been found that finer sizes can be calcined if the calcination is done in separate charges or in separate furnaces. It is said to be possible to calcine material from minus 80-mesh to 200-mesh size.

The size of the reactors will be limited by the diameter of the constriction plate, and it is expected that 100-ton capacity reactors will be about the limit. A five-furnace plant to make 500 tons a day would probably have better fuel economy than a rotary kiln and would give flexibility of operation. The life of the lining should be many years.

There is no flow of material downward through the holes in the constriction plate, as the upward currents of hot gases prevent this. There are no suction fans on the outlet gases, which flow through the dust collectors by the internal pressures set up in the kiln by the flow of hot air and by the liberation of CO_2 from the stone. There has been no soot or off-colour materials. The amount and the temperature of CO_2 issuing from the kiln can be controlled within narrow limits.

Spectrographic Analysis of Portland Cement.

IN a recent number of the Journal of Research of the United States National Bureau of Standards, Mr. A. W. Helz and Mr. B. F. Scribner describe a rapid spectrographic method for determining the amounts of the minor metallic elements in Portland cement. The probable error in a single determination is said to be less than 3 per cent. of the oxide concentration for aluminium, iron, magnesium, manganese, and titanium, 5 per cent. of the Na_2O concentration, and 8 per cent. of the K_2O concentration. Other minor elements, such as lithium, strontium, chromium, zirconium, and vanadium, may readily be included. The results of the spectrographic analyses of 21 Portland cements are compared with the results of chemical analyses in estimating the accuracy. Features of the procedure are the employment of pellets consisting of the cement powder, with graphite as a binder, cobalt oxide as an internal standard, and potassium nitrate as a buffer. The pellet is used as an electrode for excitation by an overdamped condenser discharge. The spectrum is photographed with a step sector and a diffusing screen for obtaining uniformity of illumination.

It seems possible to extend the method to the analysis of the raw materials of cement if reliable samples of the materials are available.

Recent Research on the Chemistry of Portland Cement.

A REVIEW of some of the more important advances that have been made in the chemistry of Portland cement in the period 1942 to 1946 is given by Mr. Robert H. Bogue in the Journal of Research of the United States National Bureau of Standards for August 1947. The author summarises his conclusions as follows.

(1) The stable potash compound (or solid solution) in a cement mixture, consisting of K_2O, CaO, MgO, Al_2O_3, Fe_2O_3 and SiO_2, has the composition $KC_{23}S_{12}$. When SO_3 is present the potash combines with it preferentially to form K_1SO_4.

(2) The soda of cement, in a mixture consisting of Na_2O, CaO, Al_2O_3, and SiO_2, may crystallize in the form of NC_8A_3, or a solid solution of that phase in C_3A ; a solid solution of a soda-bearing phase in αC_2S ; or inclusions of a soda-bearing phase in βC_2S.

(3) The iron-bearing phase in Portland cement is a solid solution of C_2F in a hypothetical C_2A, which may extend beyond the composition C_4AF and reach an end composition at C_6A_2F.

(4) The prismatic dark-interstitial phase of clinker is a metastable form of tricalcium aluminate possibly containing a small amount of alkali in solid solution.

(5) The α–β inversion temperature of dicalcium silicate is probably 1,456 deg. C.

(6) The β–γ inversion of dicalcium silicate may be prevented by 1-mol. per cent. additions of P_2O_5, As_2O_3, V_2O_5, Cr_2O_3, B_2O_3, or Mn_2O_3.

(7) Tricalcium aluminate has a cubic unit cell having $a_0 = 15{\cdot}24$ Å and 24 molecules.

(8) αC_2S has a hexagonal symmetry, stable at a high temperature. Under proper conditions this may be obtained at low temperature. αC_2S is βC_2S, whose twinning is caused by the inversion and whose inclusions are the result of ex-solution of dissolved phases.

(9) An $\alpha' C_2S$ exists, having the structure of βK_2SO_4. It is stable between the stability range of the α and the β forms.

(10) Hexagonal C_3A-hydrate does not exist. The material previously designated as such is a mixture of C_2A aq. and C_4A aq.

(11) In steam at temperatures above 200 deg. C. the isometric C_3AH_6 is changed into birefringent phases of two forms.

(12) Supporting evidence is given in favour of the film theory to account for the reactions of setting.

(13) Each cement has a gypsum requirement for optimum retardation that is characteristic of the cement.

(14) Calcium sulphoaluminate forms a series of solid solutions of high and low sulphate content, and the sulphate may be progressively replaced by hydroxyl or silicate.

(15) Spectroscopic methods are developed by which eight elements may be determined in duplicate on ten to sixteen cements by one operator in one day.

(16) Methods of electron microscopy and X-ray spectrometry show promise of useful application in cement research.

New Methods.

The results obtained from the use of new apparatus in the study of Portland cement are described.

SPECTROGRAPHIC ANALYSIS.—Methods have recently been developed by Helz[1] and by Helz and Scribner[2] by which eight elements may simultaneously be determined spectrographically. (A brief reference is made to these methods on page 29 of this number. In a later number it is intended to give further details.)

ELECTRON MICROSCOPY.—By means of the electron microscope, micrographs may be obtained at magnifications up to 25,000 diameters with high resolution (which may subsequently be many times enlarged), and electron diffraction patterns may be photographed. In the last few years the instrument has been applied successfully to many problems requiring resolution of fine structure. Eitel and his co-workers[3] have examined the hydration products of tricalcium silicate and tricalcium aluminate. More recently Katz and his associates[4] have reported the electron-micrographs of hydrated Portland cements, and also of some of the cement compounds. By this means Eitel found C_3S to give rise to hemispheres of $Ca(OH)_2$ and nodules identified as a calcium hydrosilicate. The C_3A gave hexagonal crystals identified as C_3AH_{12} and isometric crystals of C_3AH_6. Katz observed from C_3S and C_2S rhombic slabs (probably $CaCO_3$) and amorphous spherulites, and from C_3A, the same rhombic slabs, thin hexagonal plates, and spherulites. When a sulphate was present, needles and splines of calcium sulphoaluminate were observed.

Electron micrographs of the cement compounds made by McMurdie, but not published, showed no evidence of the rhombic slabs observed very commonly by Katz. The C_3A yielded hexagonal plates, as did also C_4AF and NC_8A_3. The C_3S and C_2S as well as commercial cements showed the presence of globules of gel, with fringes that suggest a possible beginning of crystallization. In the presence of gypsum, with C_3A or C_4AF, the heavy splines of calcium sulphoaluminate were conspicuous.

These results are the pioneer work, and indicate that the electron microscope is adaptable to the examination of cement hydration products. The use of electron diffraction has not been probed, but there is a probability that this also may be very useful. By this means the formation of solid solutions may be indicated, patterns of the several phases in a section may be separately obtained, and advantage may be taken of the opacity of thin films to electrons by applying the method to such films of hydration products formed on anhydrous crystals.

X-RAY SPECTROMETRY.—An X-ray spectrometer employing a Geiger counter in place of a photographic film makes possible the recording upon a chart both the intensity and spacings of the diffraction lines of a pattern. A photometer is not necessary for measuring the density of the lines, as intensity is indicated directly, and the spacings have only to be read from the chart. Many advantages

are possible with the use of this instrument. The examination of a specimen is possible in a much shorter space of time, and there are no films to be developed. The unique possibility presents itself of placing the sample in a small furnace inserted in the instrument, so that the X-ray pattern of materials at high temperatures may be determined. Such a furnace has been successfully made and operated by McMurdie and van Valkenburg at the National Bureau of Standards. Its use may be of the highest importance in studies on the crystal structure of compounds, inversion temperatures and solid solutions.

REFERENCES.

[1] A. W. Helz, J. Research NBS **24**, 129 (1945).
[2] A. W. Helz and B. F. Scribner, J. Research NBS **38**, 439 (1947).
[3] O. E. Radezewski, H. O. Muller, and W. Eitel, Naturwiss., **27**, 807, 837 (1939).
[4] C. M. Sliepoevich, L. Gildart, and D. M. Katz. Ind. Eng. Chem. **35**, 1178 (1943).

Packing and Despatching Cement from a Riverside Works.

A NEW plant for the despatch of cement by water and railway has been built at Memphis, Tennessee, by the Missouri Portland Cement Company, and is described by Mr. Walter C. Muellar in "Pit and Quarry" for October 1947.

Cement is brought in bulk to the plant by seven cargo barges, each with a capacity of 1,330 tons. The barges are loaded at the Company's dock on the Mississippi river, and are towed to Memphis two or three at a time by tugs which make a round trip in eight or nine days. The barges are equipped with facilities for discharging their own cargoes. A hopper bottom allows the material to flow into the path of a cable-drawn drag bucket, which delivers the material into a hopper over an 8 in. stationary pump with a pumping rate of 60 tons per hour through an 8 in. pipeline 1,000 ft. long. Air is supplied from a captive barge by a rotary air compressor delivering 1,600 cub. ft. per minute at 30 lb. pressure. This compressor is driven by two diesel engines operating at 1,500 revolutions per minute, and developing 180 h.p.

The dock consists of a two-span bridge which carries the pipelines, power cables, and walkway from the high bank to the river pier. Stairways and landings on the pier provide access to the captive barge. Air is delivered from the captive barge to the cement barge by means of a flexible hose, and the cement leaves the barge through a second flexible rubber hose and is taken to storage through the 1,000 ft. pipeline.

The storage structure (Fig. 1) consists of nine silos and four interstices and has storage space for 15,000 tons. The height is 131 ft.; the upper 85 ft. is storage space, the lower 46 ft. comprising four floors which accommodate the packing and bag departments. A feature of the silos are the steel conical bottoms, each of which has a rotary feeder, a combination which completely empties the silos without manual assistance. The height of the silo discharges makes it possible to convey material directly to the packing machines without elevating.

The packing department consists of three packing machines with independent equipment. The flow of material is directly from the silos to the packing bin, where the feed is automatically controlled. The packing machines are of the 4-tube type with a capacity of 50 tons per hour. Push buttons on the front of the machines allow the operator to control all the equipment. Each piece of equipment is connected to a dust arrestor. Dust from this arrestor, as well as from the packing machines and belt conveyor, is collected by 9 in. screw conveyors, screened

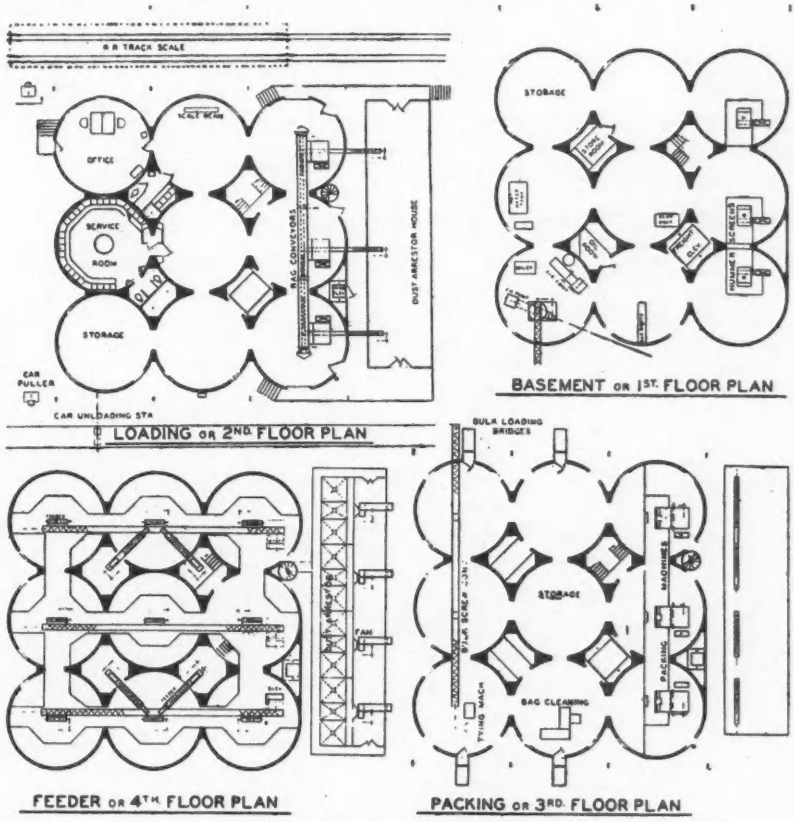


Fig. 1.—Floor Plans of Storage and Despatch Building.

by a 3 ft. by 5 ft. screen, and returned by a 10 in. by 6 in. bucket elevator to the packing bin.

Bulk loading is by means of spouts and a hose connected directly to the hoppers of the silos adjacent to the loading tracks. A rotary valve is used to control the flow. Cement may also be loaded to wagons by screw conveyors.

In the basement of the silos is the storage for paper bags, which are received by chutes from box wagons. They are taken to the packing floor on four-wheel trucks on a lift with a capacity of 3,000 lb. Returned jute sacks are taken to the packing floor where they are cleaned by means of a suction-pipe cleaner connected to a dust arrestor identical with that serving the packing machines.

The Cement Industry Abroad.

FROM time to time we have given particulars of the rate of production of cement in various countries and figures are now available, mainly in recent numbers of "Cemento-Hormigon," showing the growth of the cement industry in, among other countries, those of South America. In the following we also give some notes on China and Poland.

The Development of the Cement Industry in South America.

ARGENTINA.—Before 1914 there was only one cement works in the Argentine and this produced about 3,000 tons annually. By 1919 three works were in operation producing nearly 170,000 tons a year. By 1939 the number of works had increased to eleven, having an annual capacity of nearly two million tons and producing over one million tons each year. As reported in our number for March 1947, the annual production of just over a million tons was continued throughout the war and has been maintained since. No cement has been imported or exported since 1942.

Cement works in the Argentine favour the use of fuel oil, which is abundant at a low price. Between 0.22 ton and 0.29 ton of fuel oil is required for one ton of cement. In 1939 the amount of fuel oil, including diesel oil, used was more than 200,000 tons and fewer than 5,000 tons of coal were used in cement manufacture. A small amount of coke and wood was used. During the war less oil and more coal was used, and in 1945 the amount of oil of all kinds used was 120,000 tons, and of ordinary coal more than 50,000 tons. About 56,000 tons of soft coal and about the same amount of wood were used as fuel in cement works in 1945, as well as more than 100,000 tons of husks of grain, about 8,000 tons of sunflower seeds, and nearly 2,000 tons of maize, residues from cotton, flax and rice, and other materials. In 1946 the pre-war conditions were more nearly approached, the amount of oil used being about 210,000 tons. There were used, however, more than 15,000 tons or ordinary coal, more than 25,000 tons of soft coal and more than 40,000 tons of wood. The consumption of husks of grain as fuel had fallen to about 2,000 tons, sunflower seeds to about 4,000 tons, and other materials to about 1,000 tons.

BRAZIL.—As reported in our number for March, 1947, the cement works in Brazil appear to be working to the full capacity of about three-quarters of a million tons a year. This rate has been maintained since 1940. In 1935 the annual production was about half a million tons per year.

COLOMBIA.—The annual production of cement in Colombia has risen from less than 100,000 tons in 1935 to 250,000 tons in recent years.

CHILE.—The annual production of cement in Chile recently has been nearly half a million tons. In 1936 it was about half this amount.

PERU.—From 75,000 tons in 1936, the annual production of cement in Peru has increased to more than 250,000 tons.

URUGUAY.—In 1935 the production of cement was about 100,000 tons and is now more than 200,000 tons a year.

OTHER COUNTRIES.—The growth of the cement industry in other countries in South America shows similar increases, but generally on a smaller scale. According to the most recent figures available, the estimated annual production in Venezuela exceeds 100,000 tons, which is three times the amount in 1936.

In 1936 the annual production of cement in Bolivia was about 10,000 tons. By 1939 this amount was more than doubled and is now almost trebled.

The capacity of the cement works in Ecuador is 45,000 tons a year.

Cement in China.

IN a description, in the Journal of the American Concrete Institute, for January 1948, of the concrete industry in China, Mr. J. S. Cotton gives some particulars of the cements used in that country.

Portland cement in China is native-made, or made at works, or is imported. Imported cement is used mainly near the coast only. Native-made cement is made by mixing powdered limestone and clay and moulding the mixture into pellets by hand. The pellets are dried in the sun and then laid between layers of coal in a crude brick kiln wherein the material is fired. The product is ground by various means, but generally by rolling a heavy rock wheel over the clinker. This cement, which makes fairly strong concrete but lacks uniformity, is made largely in mountainous Western China and is used primarily for masonry.

There are only a few cement works in China, the most important being at Chungking, Shanghai, and Canton. There are two in Manchuria. The quality of the cement varies considerably. Typical results of tests of a cement from a works in Western China are : specific gravity, 3.117 ; setting-time by Vicat apparatus 2 hours 18 minutes initial and 3 hours 59 minutes final ; tensile strength of 1 : 3 mortar, 221 lb. per square inch at 7 days and 282 lb. per square inch at 28 days ; compressive strength of 2 in. by 4 in. cylinders of 1 : 3 mortar, 1,144 lb. per square inch at 7 days and 1,532 lb. per square inch at 28 days.

The greatest difficulty is the variation in fineness. The following is typical of the wide variations which occur : percentages retained on U.S.A. Sieve No. 50, 1.34 to 7.51 ; on No. 100, 5.51 to 32.51 ; and on No. 200, 14.95 to 37.78..

Some works deliver cement in wooden barrels which at times are leaky, while works on the coast and in Manchuria use paper bags. The cost of cement and transport is very high. Cement is generally transported by small boats, pack animals, lorries, or railways wagons. The loss due to leaking and damage by rain may be 5 per cent. or more since only straw matting is used to protect the cement. Poor conditions of storing may cause a further loss due to damage by rain and damp.

Cement Production in Poland.

IN the year 1947 the Polish cement industry produced 1,450,000 tons of Portland cement. It is anticipated that the pre-war rate of production, namely, 1,700,000 tons, will be reached in the year 1948.

The New British Standards for Cements.

THE British Standards for ordinary and rapid-hardening Portland cements, Portland-blastfurnace cement, and high-alumina cement were revised recently and a new specification for low-heat Portland cement was published.

Ordinary and Rapid-hardening Portland Cement.

THE following are the requirements of the new specification for ordinary and rapid-hardening Portland cement, B.S. No. 12, 1947, which differ from those of the previous (1940) specification.

The chemical composition is unaltered except that the upper limit for the amount of lime has been slightly raised. The amount of lime, after deducting that necessary to combine with the sulphuric anhydride, must be such that the value of the expression $\frac{CaO}{2{\cdot}8SiO_2 + 1{\cdot}2Al_2O_3 + 0{\cdot}65Fe_2O_3}$ is not greater than 1·02 and not less than 0·66, when the amounts of lime, silica, alumina, and ferric oxide are expressed as percentages. A method which is the same as that, given in the following, for low-heat Portland cement (B.S. No. 1370, 1947), for determining the percentage of the insoluble residue, is given.

The requirements for strength are unaltered. The tensile test is retained, but a new machine for conducting the optional compressive test on mortar cubes is briefly described and illustrated in the same manner as in B.S. No. 1370. The specification and working drawings for this machine are published separately.

The amount of water (P) in a cement paste of standard consistency, which replaces the normal consistency described in previous specifications, is used as the basis for determining the percentages required for the specimens in various tests. Thus the amount of water to be used for gauging the cement paste for the test for setting time is $0{\cdot}85P$, which is slightly more than in the superseded standard; for the soundness test it is $0{\cdot}78P$, which corresponds to the previous "normal consistency" and which is unaltered. The amount of water to be used for gauging 1 : 3 mortar for the test for tensile strength is, as before, $0{\cdot}195P + 2{\cdot}5$. A table gives the values of P from 26 per cent. to 33 per cent. The requirements for the tests for soundness and setting times are the same as before, but the setting times for quick-setting cement are omitted.

The permeability test, described in B.S. No. 1370, and given later in this article, for assessing the fineness by measuring the specific surface is included in the new standard. The sieving test is retained, although it only measures the amount of coarse material. Either test may be used. The maximum residues by weight on a B.S. sieve No. 170 conform to those specified in the previous edition of B.S. No. 12, that is 10 per cent. for ordinary Portland cement and 5 per cent. for rapid-hardening Portland cement. If the permeability test is used the specific surface must be not less than 2,250 sq. cm. per gramme for ordinary Portland cement and 3,250 sq. cm. per gramme for rapid-hardening Portland cement.

The clauses in the new standard have been re-arranged and in some cases are shorter because descriptions of the methods of carrying out the tests are given in

appendixes. Some minor revisions have been made to the phraseology of some clauses that are otherwise unaltered.

There are some alterations in the requirements regarding manufacturers' certificates and the cost of tests. The manufacturer must satisfy himself that the cement conforms to the requirements of the Standard and, if requested to do so, must give the purchaser a certificate to this effect. If the purchaser requires independent tests the samples are to be taken, at the option of the purchaser, before or immediately after delivery. The manufacturer must supply free of charge the cement required for the tests and, unless otherwise specified in the enquiry and order, the manufacturer must bear the costs of the tests if the cement does not comply with the Standard.

Portland-blastfurnace Cement.

The revised Standard for Portland-blastfurnace cement (B.S. No. 146, 1947) conforms, where applicable, to the revisions in B.S. No. 12, 1947. The fineness as determined by B.S. sieve No. 170 is unaltered, that is the maximum residue is 10 per cent., but the optional permeability test, now included, must show that the specific surface is not less than 2,250 sq. cm. per gramme, which is the same area as for ordinary Portland cement.

High-alumina Cement.

The revisions to the Standard for high-alumina cement (B.S. No. 915, 1947) also conform in general with those, where applicable, made to B.S. No. 12, 1947. There are no alterations to the physical or chemical requirements, but the optional permeability test for fineness is included ; the specific surface as determined by this test must not be less than 2,250 sq. cm. per gramme.

Low-heat Portland Cement.

A new British Standard, No. 1370, 1947, gives the requirements of a type of Portland cement intended for structures where large volumes of concrete have to be placed, such as dams, bridge abutments, and large retaining walls. In such masses of concrete there is often a considerable rise in temperature due to the heat evolved as the cement sets and the slow rate at which the heat is dissipated from the surface. The contraction which occurs on subsequent cooling induces tensile stresses in the concrete which may result in cracking. A cement of the type covered by the new specification evolves less heat than ordinary or rapid-hardening Portland cement. The rate at which strength is developed in a low-heat Portland cement is lower at early ages than that in ordinary Portland cement, but the strength at greater ages is not reduced.

The main innovations in this specification include the definition of fineness by the measurement of the specific surface, that is the superficial area of a unit weight of the cement ; a test for the total amount of heat of hydration evolved after 7 and 28 days ; the maximum permissible lime content is lower than in B.S. No. 12, 1947, since a high lime content is not compatible with a low heat evolution ; the tensile test is omitted ; and a method for determining the insoluble residue is specified. The principal requirements of the specification are given in the following.

The composition and manufacture of the cement are similar to those for ordinary cement, including the prohibition of the addition of any material, including slag, after burning other than calcium sulphate or water. The general requirements regarding sampling, testing, and the cost of tests are also in accordance with B.S. No. 12, 1940, the arrangement of the clauses in which differ from, and the requirements are slightly different from, B.S. No. 12, 1947.

FINENESS.—The cement when tested by the method described later must have a specific surface of not less than 3,200 sq. cm. per gramme.

CHEMICAL COMPOSITION.—The chemical composition of the cement must comply with the following. The percentage of lime, after deduction of that necessary to combine with the sulphuric anhydride present, must be not more than 2·4 times the percentage of silica plus 1·2 times the percentage of alumina plus 0·65 times the percentage of iron oxide ; the percentage of lime must be not less than 1·9 times the percentage of silica plus 1·2 times the percentage of alumina plus 0.65 times the percentage of iron oxide (compare with the formula for the maximum percentage of lime in B.S. No. 12, 1947). The ratio of the percentage of alumina to that of iron oxide must be not less than 0.66 ; The weight of insoluble residue, as determined by a method described later, must not exceed 1 per cent. and the magnesia must not exceed 4 per cent. The total sulphur content calculated as sulphuric anhydride (SO_3) must not exceed 2.75 per cent. and the total loss on ignition must not exceed 3 per cent. for cement manufactured or sampled or tested in temperate climates, and 4 per cent. for cement manufactured or sampled or tested in hot climates.

STRENGTH.—The average compressive strength of not less than three mortar cubes prepared, stored, and tested in the standard manner must be not less than 1,000 lb. per square inch at 3 days, not less than 1,600 lb. per square inch at 7 days, and at 28 days the strength must be higher than that at 7 days and not less than 3,750 lb. per square inch.

SETTING TIME.—The initial setting time of the cement when tested in accordance with the standard method must be not less than one hour, and the final setting time not more than ten hours.

SOUNDNESS.—The cement when tested for soundness by the Le Chatelier method, must have an expansion of not more than 10 mm. In the event of the cement failing to comply with this requirement, a further test must be made from another portion of the same sample after it has been aerated by being spread out to a depth of 3 in. at a relative humidity of 50 per cent. to 80 per cent. for seven days. The expansion must then not exceed 5 mm.

HEAT OF HYDRATION.—The heat of hydration, when tested by the method described later, must be not more than 65 calories per gramme at 7 days and not more than 75 calories per gramme at 28 days.

CEMENT IN HOT CLIMATES.—The temperatures mentioned in the description of the tests are applicable to temperate climates. For cement intended for use in hot climates the cement may be tested at any higher temperature up to 95 deg. F. When cement is tested at temperatures above 58 deg. F. to 64 deg. F. (14·4

LIBRARY COPY
SCHOOL OF MINERAL E
University of Wa
Seattle 5, Wash.

deg. C. to 17·8 deg. C.) or, in the case of the test for heat of hydration, above 70 deg. F. (21·1 deg. C.) the setting time, the strength and the heat of hydration, may be altered if agreed between the purchaser and the vendor, since an increase in the testing temperature reduces the setting time and increases both the compressive strength and the heat of hydration.

DETERMINATION OF HEAT OF HYDRATION.—The heat of hydration is determined as follows. The calorimeter, Fig. 1, required for the determination of the heat of hydration consists of an open-mouthed vacuum flask of 1 pint capacity with a cork lid 1½ in. thick, an insulated container for the flask, a Beckmann thermometer having a range of 6 deg. C. with reading lens, a constant speed stirrer, and a funnel for the introduction of the sample.

The flask is selected so that when filled with 398 cc. of water, the surface of the water is 0·75 in. below the lower surface of the bung. Also, when the flask is filled with 400 cc. of warm water, the fall in temperature must not exceed 0·002 deg. C. per minute per degree Centigrade above room temperature, the fall being determined after standing without stirring for half an hour. The whole inner surface of the vacuum flask, the underside of the cork stopper, and the parts of the thermometer and stirrer which protrude beneath the stopper are evenly and thinly coated with paraffin wax, having a congealing point of about 60 deg. C., thus forming an acid-proof lining. Should the lining become damaged the whole lining must be renewed. The container has an insulating layer of cork, cotton wool, or the like, at least 1 in. thick, completely enclosing the flask, and supports the flask and the stirrer motor. The thermometer is adjusted so that the upper part of the range approximates to 22 deg. C., and is rigidly held by the cork stopper so as to avoid accidental contact with the blades of the stirrer. To facilitate removal of the thermometer the stopper may be halved, one part supporting the thermometer and the other the funnel. The glass stirrer is of the double-bladed propeller type, approximately 1½ in. diameter, and extends to within 1½ in. of the bottom of the flask. Means are provided for disconnecting the stirrer from the motor, which is a synchronous motor geared to run at a constant speed of about 400 r.p.m. The heat developed by the stirrer when running continuously must not be more than 0·4 calorie per minute. The funnel is of the Gooch type with a stem of ¼ in. internal diameter and a body about 1 in. long and 1 in. diameter. The stem must not protrude more than ⅛ in. beneath the cork stopper.

The materials used in the test must conform to the following. The 2N(±0·05) nitric acid for the solution test must be made up in bulk from A.R. quality materials. Whenever a new batch is prepared the heat capacity of the calorimeter must be re-determined. The hydrofluoric acid is 40 per cent. w/w A.R. quality. For the determination of the heat capacity A.R. quality zinc oxide is required.

Determination of the Heat Capacity.—The wax lining is inspected for faults and 9·6 cc. (± 0·1) of hydrofluoric acid and 388 cc. (± 0·1) of 2·0 N. nitric acid are then measured into the calorimeter at a temperature of 18 deg. C. For convenience in measuring these quantities a standard flask of 388 cc. capacity, calibrated at 18 deg. C. is constructed. The hydrofluoric acid is measured in a

small measuring cylinder made by sealing a 15 cm. length of 1-cm. diameter polythene resin tube to a flat plate of the same material. Enough zinc oxide for about six determinations is ignited for one hour at 900 deg. C. to 950 deg. C., cooled in a desiccator containing anhydrous calcium chloride, and ground to pass a B.S. sieve No. 60. For each determination about 7 gm. of this ignited oxide is again heated to 900 deg. C. to 950 deg. C. for five minutes, and is then cooled for at least 2½ hours and not more than five hours in the calcium chloride desiccator before weighing accurately. The calorimeter is assembled and the stirrer run for

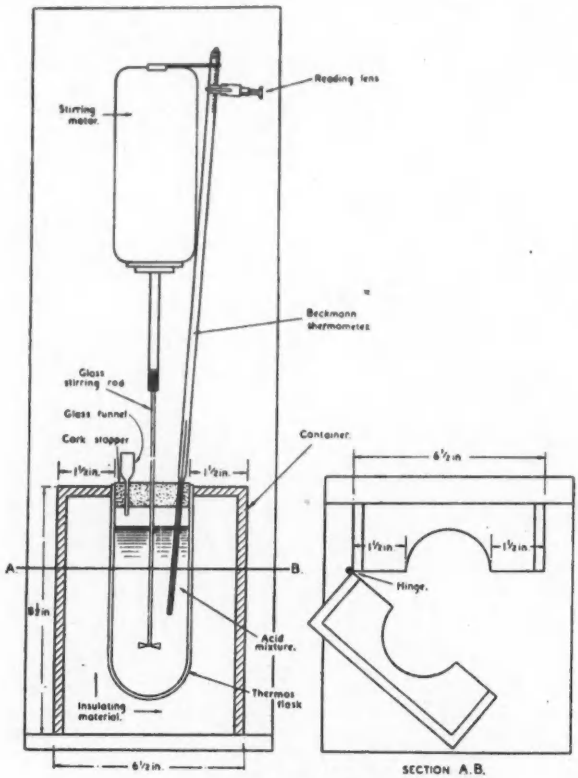


Fig. 1.—Details of Calorimeter.

at least five minutes to allow the temperature to become uniform. Temperature readings correct to 0·001 deg. C. are then taken every minute for five minutes to determine the initial heating or cooling correction. The zinc oxide is introduced through the funnel steadily over a period of 1 to 2 minutes; the funnel is then brushed clean with a camel-hair brush. Readings of the temperature are

continued at one minute intervals until the solution is complete, as indicated by a steady rate of heating or cooling of the calorimeter. The solution period should not exceed 20 minutes. Readings are continued for a further five minutes, to determine the final heating or cooling correction. The initial and final heating or cooling rates are then plotted against the corresponding calorimeter temperatures, and the two points joined by a straight line. From this graph the corrections are read for each temperature reading during the solution period. These corrections are summed and the total added or subtracted as appropriate to the observed rise in temperature.

The heat capacity in calories per degree is calculated from

$$\frac{\text{Weight of ZnO (gm.)}}{\text{corrected temperature rise}} \left\{ 259{\cdot}1 - (0{\cdot}2\,\theta \times 0{\cdot}1\,\theta_0) \right\}$$

where θ is the final temperature of the calorimeter and contents in degrees C., and θ_0 is room te mperature in degrees C.

Preparation of Cement.—A sample of the cement weighing 60 gm. and 24 cc. of distilled water is mixed by hand for four minutes and then filled into three glass specimen tubes each 1½ in. by ¾ in. and sealed with wax and corked. The temperature of the mixing water must be between 15 deg. and 25 deg. C. The specimen tubes are stored in a vertical position at 70 deg. F. until the time of test.

Determination of the Heat of Solution.—For the determination of the heat of solution of unhydrated cement, a sample of about 3 grammes is weighed out, approximately 7 gm. being weighed out at the same time for the determination of the loss on ignition. The determination of the rise in temperature is then carried out as described for zinc oxide. The heat of solution of unhydrated cement in calories per gramme is $\frac{\text{Heat capacity} \times \text{corrected temperature rise}}{\text{weight of sample corrected for loss on ignition}} - 0{\cdot}2\,(\theta_0 - \theta)$. The mean of three determinations carried out within seven days of the mixing of the hydrated samples must be taken.

For the determination of the heat of solution of the hydrated cement, one of the glass vials is broken open and all adherent wax and glass removed from the cement, which is then ground (as rapidly as possible to avoid carbonation) to pass a B.S. sieve No. 18. The ground sample is kept in a stoppered weighing bottle from which samples of 4·2 gm. and 7 gm. for tests for heat of solution and loss on ignition respectively are weighed out. The loss on ignition is determined on each sample used for the heat-of-solution test. The determination of the rise in temperature is carried out as before. The heat of solution of hydrated cement, in calories per gramme of ignited weight, is

$$\frac{\text{Heat capacity} \times \text{corrected temperature rise}}{\text{weight of sample corrected for loss on ignition}} - 0{\cdot}4\,(\theta_0 - \theta).$$

The mean of three determinations on separate sample vials must be taken.

Heat of Hydration.—The heats of hydration are determined at seven and 28 days by subtracting the respective heats of solution from the heat of solution of the unhydrated cement. Heats of solution are calculated to the nearest 0·1 calorie and heats of hydration to the nearest calorie.

LOSS ON IGNITION.—The samples are placed in a cool furnace and the temperature raised over a period of one hour to 900 deg. C. After 3 to 4 hours at 900 deg. C., the sample is cooled in a desiccator containing anhydrous calcium chloride and weighed after half an hour. All weighings should be correct to the nearest milligramme.

Determination of Insoluble Residue.

One gramme of cement is weighed into a 250-ml. to 400-ml. beaker and stirred with 40 ml. of water; 10 ml. of concentrated HCl having a specific gravity of 1·16 are added and the mixture is stirred again. The mixture is warmed, any lumps present being broken up, and boiled for ten minutes, maintaining constant volume, stirring if necessary. The contents of the beaker are then filtered, the beaker is rinsed out five times with hot water, and the residue on the filter washed about ten times with hot water. The residue is then washed from the filter-paper back into the same beaker with about 30 ml. of hot water and boiled for ten minutes with 30 ml. of 2 Normal Na_2CO_3 solution, maintaining constant volume. The contents of the beaker are then filtered again through the same filter paper and washed at least five times with water, taking care to transfer all the residue to the paper, and is then washed with a little 2 Normal HCl solution and finally with water until free from chlorides. The filter paper with the residue is then dried, ignited, and weighed as "insoluble residue."

This test is included in the Standards for ordinary, rapid-hardening, and low-heat Portland cements.

Permeability Test for Fineness.

This test determines the fineness of the cement as represented by the specific surface expressed as the total superficial area in square centimetres per gramme. The apparatus consists of a permeability cell, a manometer, and a flowmeter.

PERMEABILITY CELL.—The cell consists of a phosphor bronze, stainless steel, or brass cylinder made in two parts bolted together by means of flanges and containing a perforated plate on which is supported a No. 40 filter paper 3·2 cm. diameter. A rubber or other gasket renders the joint airtight. By means of a plunger the cement sample is formed into a cylindrical bed supported by the filter paper. The dimensions are shown in Fig. 2. The filter paper must be changed after every six determinations.

MANOMETER STAND.—The permeability cell is connected by rubber bungs to a manometer and flowmeter as shown in Fig. 3. The arms of the manometer should be about 60 cm. long and the value of the constant C (as defined in the following) of the capillary of the flowmeter must be from 2·0 to 4·0 $\times$ 10^{-6} c.g.s. units. The bore of the capillary must be not less than 0·5 mm. The liquid in both U-tubes is paraffin. The flow of air may be produced by any convenient process, but the air entering the apparatus must be dried by passing through a tower packed with anhydrous calcium chloride or other suitable desiccant.

CALIBRATION OF THE FLOWMETER.—Dry air is passed through the flowmeter at a constant rate for a known time. The air issuing therefrom is collected over water and the amount is measured. This is repeated for a number of manometer

readings over the range from 25 cm. to 55 cm. The average value of the constant C is calculated from $C = \frac{Qn}{h_2 d_L}$, where Q is the volume (c.c.) of dry air passed in one second corrected to atmospheric pressure. If the measured volume of air is V c.c. at atmospheric pressure P, and the vapour pressure of water at the room temperature is p, and the time during which the air is collected is t seconds, $Q = \frac{V}{t} \frac{(P - p)}{P}$. The viscosity of air in c.g.s. units at the given temperature is n; h_2 is the manometer reading in centimetres; and d_L is the density of the liquid in the manometer. The constant C must be checked every three months.

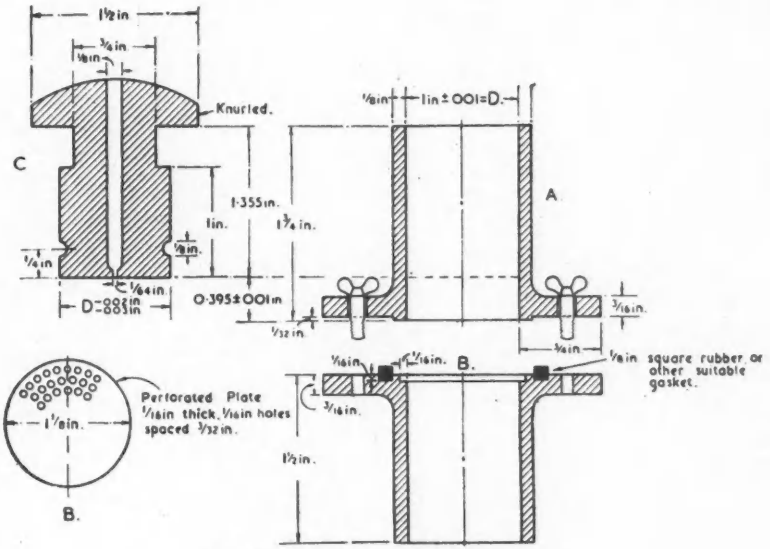


Fig. 2.—Details of Permeability Cell.

The viscosity of air in c.g.s. units multiplied by 10^{-4} at temperatures from 15 deg. C. to 25 deg. C is

Temperature deg. C.	15	16	17	18	19	20	21	22	23	24	25
Viscosity (n) ..	1·78	1·78	1·79	1·79	1·80	1·80	1·81	1·81	1·82	1·82	1·83

Readings of the manometer should not differ by more than 0·05 cm. in a period of one minute.

DETERMINATION OF DENSITY.—The density of the cement is determined in the usual manner by displacement of a liquid in a density bottle. The liquid must be redistilled paraffin and the bottle containing the weighed cement must be half filled with paraffin and evacuated for at least half an hour on the water pump before the bottle is filled with paraffin and transferred to a thermostat. The accuracy of the density determination must be within 0.01 g. per cubic centimetre.

DETERMINATION OF SPECIFIC SURFACE.—From Table 1 a weight of cement is selected which will give when compacted a porosity of 0·475 at the known density of the cement. The porosity is defined as the ratio of the volume of pore space to the total volume of the bed. The cement is brushed from the weighing bottle into the permeability cell, which is gently shaken from side to side to level the surface. If the cement is lumpy, it may first be rubbed gently with a spatula on glazed paper. The cell is then tapped four times by allowing it to fall from a height of about 1 cm. on to a wooden bench. The plunger is slowly

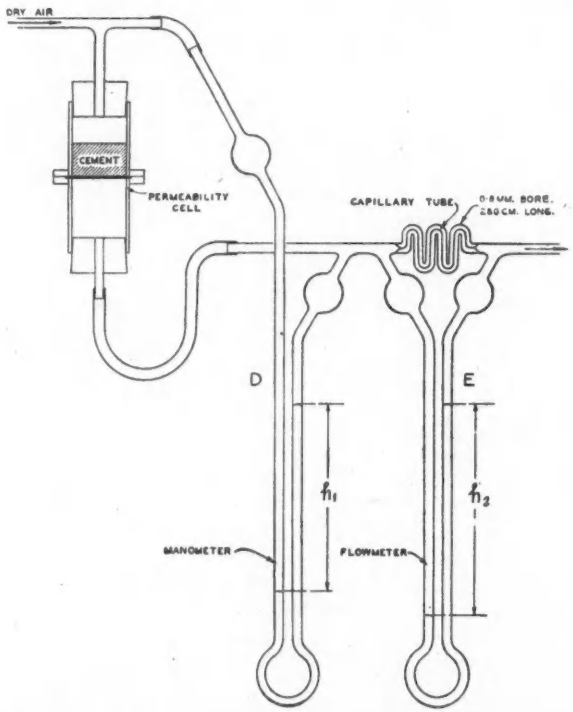


Fig. 3.—Permeability Apparatus with Manometer and Flowmeter.

inserted and pushed home so that the collar of the plunger is in contact with the top of the permeability cell. The plunger must not be twisted while in contact with the cement but must be slowly withdrawn with a twisting motion. If the bed of cement is seen to be disturbed it must be knocked out and the operation repeated. Occasionally a cement is encountered which springs up slightly on withdrawing the plunger. The increase in the depth of bed so caused may be up to 0·01 cm. The resulting error in specific surface will be less than 2 per cent., but

if desired the true depth of the bed may be measured and the result corrected. The upper bung is then inserted and the air turned on slowly; the lower bung is next inserted slowly in order to avoid forcing air through the cement in the wrong direction. The rate of air flow is adjusted until the flowmeter shows a difference in level of from 30 cm. to 50 cm. Readings of the difference in level h_1 of the manometer and of the difference in level h_2 of the flowmeter are then made. These observations are repeated until a constant ratio of h_1 to h_2 is obtained.

The specific surface Sw is given by $K\sqrt{\frac{h_1}{h_2}}$, where K is $\frac{14}{d(1-\epsilon)}.\sqrt{\frac{\epsilon^3 A}{CL}}$, in which ϵ is the porosity, that is 0·475, A the area (sq. cm.) and L the length (cm.) of the cement bed, d is the density of the cement, and C the flowmeter constant. Values of K for densities between 2·8 and 3·2 should be tabulated for each apparatus. For apparatus made to the specified dimensions, K is $19{\cdot}65\frac{1}{d}\sqrt{\frac{1}{C}}$, the values of A and L being 5·066 sq. cm. and 1 cm. respectively. The depth of bed shown in Fig. 2 is 0·001 in. greater than 0·394 in. (1 cm.) in order to allow for the filter

TABLE 1.—WEIGHT OF CEMENT (GRAMMES) REQUIRED TO FORM A BED 1 CM HIGH AND 2·54 CM. DIAMETER (POROSITY 0·475)

Density	0	1	2	3	4	5	6	7	8	9
2·8	7·449	7·475	7·502	7·528	7·555	7·582	7·608	7·634	7·661	7·688
2·9	7·715	7·741	7·768	7·794	7·821	7·848	7·874	7·901	7·927	7·954
3·0	7·980	8·007	8·034	8·060	8·087	8·114	8·140	8·167	8·193	8·220
3·1	8·247	8·273	8·300	8·326	8·353	8·380	8·406	8·433	8·459	8·486
3·2	8·512	8·539	8·566	8·592	8·619	8·646	8·672	8·700	8·725	8·752

paper which is compressed where it is held by the walls of the metal cylinder but not in the cell itself. These dimensions should be checked by means of a travelling microscope or by using a gauge to simulate the cement bed. The gauge is of hardened steel, 0·99 in. diameter and 0·3987 in. high. It is placed on the filter paper and the plunger is inserted. The gap between the shoulder of the plunger and the top of the permeability cell is checked by feeler gauges, and should be 0·005 in. The dimensions of the permeability cell must be checked after every hundred determinations.

The permeability test for fineness applies to all the revised British Standards, that is B.S. Nos. 12, 146, 915, and 1370 (1947).

The foregoing extracts from the Standards are published by permission of the British Standards Institution from which copies of the complete specifications (price 3*s*. 6*d*. each) can be obtained.

Summaries of British Standards.

AMONG the 240 summaries of British standards given in the new edition of the "Handbook of British Standards for Building Materials and Components for Housing" (London: British Standards Institution, 1947. Price 21s.), are those for ordinary, rapid-hardening, and Portland blastfurnace cement; high-alumina cement; quicklime and hydrated lime; gypsum and anhydrite building plasters; and pigments for colouring cement, magnesium oxychloride, and concrete. Particulars of revisions of standards and of standards published since 1946 are given in a leaflet that accompanies the Handbook and in which a brief note of the standard for low-heat Portland cement is given. The references to other types of cement relate to the standards issued before 1947.

"THE CONCRETE YEAR BOOK"

The Handbook, Directory, and Catalogue of Concrete.

972 PAGES — PRICE 5s. 8d. by post.

A few copies of the

1948 EDITION

still available.

CONCRETE PUBLICATIONS LIMITED,
14, Dartmouth Street, Westminster, S.W.1.

SUPER REFRACTORIES for CEMENT KILNS

ALITE No. 1. 68% ALUMINA
Refractory Standard 3250° Fahr.

ALITE B. 57% ALUMINA
Refractory Standard 3180° Fahr.

ALITE D. 41% ALUMINA
Refractory Standard 3150° Fahr.

E. J. & J. PEARSON, LTD.,
STOURBRIDGE, ENG.

MISCELLANEOUS ADVERTISEMENTS

SCALE OF CHARGES.

Situations Wanted, 1½d. a word; minimum 3s. 6d. Situations Vacant, 2d. a word; minimum 5s. Box number 6d. extra. Other miscellaneous advertisements, 5s. minimum.

Advertisements must reach this office by the 5th of the month of publication.

WANTED. New or secondhand 3 phase 50 cycles outdoor type transformer ratio 22.0/3.3 KV. Transformer to work in 46°C. ambient temperature. Complete with conservator, breather, lugs, rating plates, thermometer pockets, and other accessories. Aggregate capacity of one or more units required about 3,000 KVA. Send complete particulars and price to Dalmia Cement Ltd., New Delhi, India.